Journal of Advanced Ceramics
2014, 3(2): 132–136
DOI: 10.1007/s40145-014-0103-3
ISSN 2226-4108
CN 10-1154/TQ
Research Article

Preparation of titanium phosphate white pigments with titanium sulfate and their powder properties

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Received: December 31, 2013; Revised: March 14, 2014; Accepted: March 18, 2014

Abstract: Titanium oxide that has photocatalytic activity is used as white pigment for cosmetics. A certain degree of sebum on the skin is decomposed by the ultraviolet radiation in sunlight. In this work, as novel white pigment, titanium phosphates were synthesized with titanium sulfate and phosphoric acid for cosmetics. Their chemical composition, powder properties, photocatalytic activity, color phase, moisture retention, and smoothness were studied. These titanium phosphates had less photocatalytic activity to protect the sebum on the skin. Samples without heating and those heated at 100 ℃ showed high reflectance in the range of visible light. Sample prepared in Ti/P = 3/2 had higher moisture retention than samples prepared in other Ti/P ratios.

Keywords: white pigment; titanium phosphates; photocatalytic activity; smoothness

1 Introduction

As a white pigment, titanium dioxide is used for cosmetic applications [1]. This oxide is well known to have a photocatalytic activity. Therefore, a certain degree of sebum on the skin is decomposed by the ultraviolet radiation in sunlight. To repress this effect, technical processes of several kinds have been investigated and used. For example, as one such technique, composite particles with silicon oxide have been used [2,3]. However, these particle materials are too hard for use on human face. Mild materials are required for use as white pigment on human face. In addition, one report has described that microfine titanium dioxide is adsorbed through the skin [4]. A novel white pigment that is not adsorbed must be used.

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Phosphates have been used for ceramic materials, catalysts, adsorbent, fluorescent materials, dielectric substances, biomaterials, metal surface treatment, fertilizer, detergents, food additives, fuel cells, pigments, and other applications [5–7]. Phosphate materials are well known to have high affinity for living organisms. Therefore, as novel white pigment, phosphates are expected to be useful as cosmetics.

In earlier studies, we prepared a titanium phosphate pigment that has no catalytic activity with titanium chloride, $TiCl_4$ [8,9]. The obtained titanium phosphates have less photocatalytic activity to protect the sebum on the skin. The titanium chloride is difficult to treat because of the formation of smoke and undesirable precipitate. Generally, raw materials have influence on the formation and properties of materials. In the group of titanium compounds, titanium sulfate is also an important compound to obtain titanium oxide as well as titanium chloride.

In this work, titanium phosphates were prepared from titanium sulfate and phosphoric acid. Their respective chemical compositions, powder properties, photocatalytic activity, color phases, moisture retention, and smoothness of the obtained precipitates and their thermal products were studied for application to cosmetics.

2 Experimental

The 0.1 mol/L of titanium sulfate solution was mixed with 0.1 mol/L of phosphoric acid solution at room temperature for more than 1 h, respectively in molar ratios of Ti/P = 1/2, 3/4, 1/1, 3/2, 2/1, and 3/1. The precipitates were filtered off, washed with water, and dried. All chemicals were of commercial purity from Wako Chemical Industries Ltd. (Osaka, Japan) and used without further purification.

A part of the precipitates were dissolved in a sulfuric acid solution. The ratios of phosphorus and titanium in the precipitates were also calculated based on the ICP results of these solutions using an SPS1500VR from Seiko Instruments, Inc. The chemical compositions of these materials were analyzed using X-ray diffraction (XRD). The XRD patterns were recorded on an X-ray diffractometer (MiniFlex, Rigaku Corp.) using monochromated Cu Kα radiation. Samples were heated at 100 ℃ in air condition. These thermal products were also analyzed according to their XRD patterns.

The particle shapes and sizes of the precipitates as well as their thermal products at 100 ℃, were estimated based on scanning electron microscopy (SEM) images and particle size distributions. The SEM images of the titanium phosphates were observed (JGM-5510LV, JEOL). The particle size distributions of these materials were measured using centrifugal precipitation particle-size distribution (SA-CP3L, Shimadzu Corp.).

The cosmetic properties were estimated according to photocatalytic activity, color phase, and smoothness. The photocatalytic activity of the samples was estimated with the decomposition of methylene blue by 365 nm radiation [10,11]. 0.01 g of the sample was placed in 3 ml of methylene blue solution (1.0×10^{-5} mol/L), and then this solution was radiated. The decrease of the absorption at about 660 nm was estimated for 120 min. The color of phosphate pigments was estimated using ultraviolet–visible (UV–Vis) reflectance spectra (UV2100, Shimadzu Corp.). The whiteness was also estimated with TES135 plus color analyser. For the moisture retention of the samples, 0.3 g of the sample was mixed with 0.1 g of water, and the weight loss was then evaluated at 50 ℃ (MS-70 Moisture Analyzer, A and D Instruments Co. Ltd.). The same weight loss over longer time means high water retention of the samples. The particle smoothness was measured on artificial leather with KES-SE objective evaluation of surface friction property (Kato Tech Co. Ltd.). The values of MIU and MMD respectively represent the slipping resistance (coefficient of kinetic friction) and roughness of powders (dispersion on coefficient of kinetic friction). Sample powders were spread on the leather. Then a sensor ran over these powders. The values of MIU and MMD were calculated respectively from the power to move the sensor and the pitching of the sensor. The values of MIU and MMD have no unit because these values are related with coefficients of friction and scattering, respectively.

3 Results and discussion

3.1 Chemical composition and powder properties of precipitates

Table 1 shows the Ti/P ratios of the samples prepared. Samples prepared at Ti/P = 1/2, 3/4, 1/1, and 3/2 have higher Ti/P ratios than preparation conditions. On the other hand, samples prepared at Ti/P = 2/1 and 3/1 indicate lower Ti/P ratios. The stable chemical composition in these preparation conditions is not clear from ICP results. Figure 1 presents XRD patterns of samples prepared in various conditions. The weak diffractions at the angels nearby 30° are halo peaks. All samples are in amorphous state according to XRD analyses. These results are the same as those prepared from titanium chloride [9]. Titanium phosphates are easy to form amorphous state in precipitation process.

Table 1 Ti/P ratios of samples prepared with titanium sulfate

Sample	Ti/P ratio under preparation condition	Ti/P ratio of the precipitate
a	1/2	1.17
b	3/4	1.54
c	1/1	1.34
d	3/2	2.23
e	2/1	1.53
f	3/1	1.82

From the viewpoint of particle shape, spherical particles are suitable for cosmetic applications. Figure 2 portrays SEM images of samples prepared with titanium sulfate in various Ti/P ratios. No specified shape is observed in all samples. The Ti/P ratios have less influence on particle shapes.

Figure 3 presents the particle size distributions of samples prepared in various Ti/P ratios. Sample

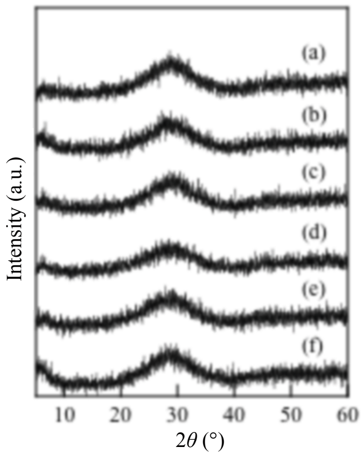

Fig. 1 XRD patterns of samples prepared in various Ti/P ratios: (a) 1/2, (b) 3/4, (c) 1/1, (d) 3/2, (e) 2/1, and (f) 3/1.

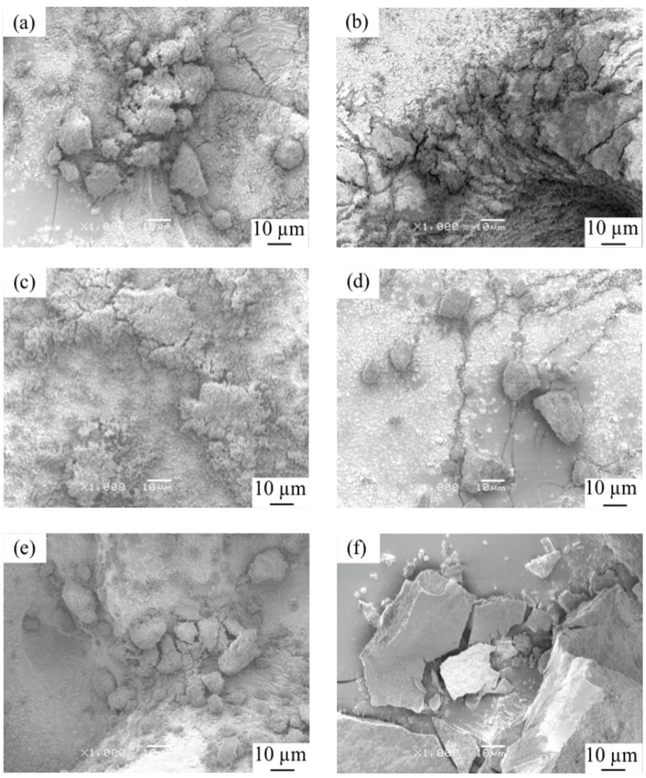

Fig. 2 SEM images of samples prepared in various Ti/P ratios: (a) 1/2, (b) 3/4, (c) 1/1, (d) 3/2, (e) 2/1, and (f) 3/1.

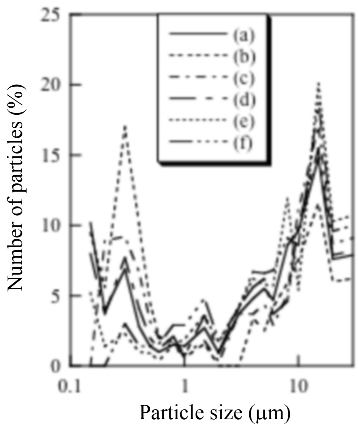

Fig. 3 Particle size distributions of samples prepared in various Ti/P ratios: (a) 1/2, (b) 3/4, (c) 1/1, (d) 3/2, (e) 2/1, and (f) 3/1.

prepared in Ti/P = 3/4 has high proportion at 15 μm and 0.3 μm in particle size distribution (b). All samples indicate high proportion at 15 μm. On the other hand, the particle proportion at 0.3 μm is low in particle size distributions of samples prepared in Ti/P = 2/1 and 3/1 ((e) and (f)). The Ti/P ratio in preparation has some influence on the particle size distribution. For cosmetic applications, small and homogeneous particles are suitable. However, overly small particles show the difficult shortcoming of entering pores in the skin [4]. The standard size of the white pigment for cosmetics is difficult to determine because the skin pore size is affected by factors such as age, gender, and climate. Furthermore, overly large particles are inappropriate because of the cracking of the coating on the skin. It is important to control the pigment particle size.

3.2 Cosmetic properties of titanium phosphates

Figure 4 shows the respective photocatalytic activities of samples prepared in various conditions. Because titanium dioxide is used as a white pigment in cosmetics, this compound is evaluated for comparison with uncoated titanium phosphate [1]. Methylene blue is decomposed with titanium dioxide using UV radiation (g). Titanium phosphate has little photocatalytic activity in spite of the kinds of Ti/P ratios ((a)–(f)). Titanium phosphate is a mild material that can protect the sebum on the skin.

Figure 5 shows UV–Vis reflectance spectra of samples prepared in various Ti/P ratios. All samples indicate high reflectance at the range of visible light. Samples heated at 100 ℃ also indicate high reflectance in this range. All samples without heating and heated at

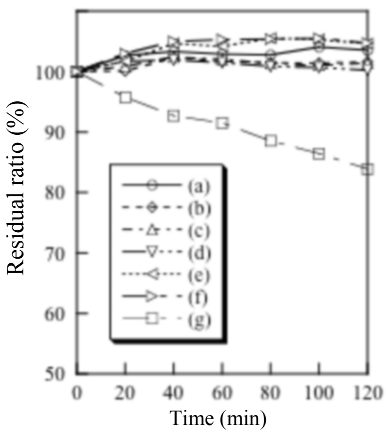

Fig. 4 Photocatalytic activity of samples prepared in various Ti/P ratios: (a) 1/2, (b) 3/4, (c) 1/1, (d) 3/2, (e) 2/1, (f) 3/1, and (g) TiO_2.

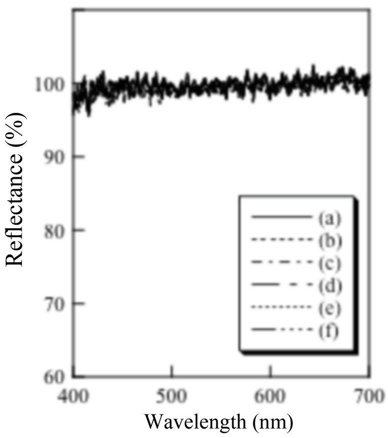

Fig. 5 UV–Vis reflectance spectra of samples prepared in various Ti/P ratios: (a) 1/2, (b) 3/4, (c) 1/1, (d) 3/2, (e) 2/1, and (f) 3/1.

100 ℃ are white powders. Table 2 shows the whiteness of samples prepared in various conditions. These values are L^* value in $L^*a^*b^*$ color space. All samples indicate high brightness in spite of the Ti/P ratios. Samples without heating have higher brightness than samples heated at 100 ℃. This color change by heating is generally related with the surface of particles, particle sizes, crystalline structure, and defect of crystalline structure. In this work, the particle size has less change by heating. Because samples without heating and heated at 100 ℃ are amorphous in XRD patterns, the crystalline structures and their defects are not clear. Therefore, the reason that samples prepared in this work become a little dark is difficult to clear.

Moisture helps to prevent the itchiness and damage to the skin. It is important that the pigments used in cosmetics retain the moisture on the skin [11]. Figure 6 shows the moisture retention of the samples prepared in various Ti/P ratios. In this analysis, the theoretical weight loss is 25% (sample 0.3 g, water 0.1 g). However, some samples have weight loss larger than 25%. At the same weight loss, the longer time indicates higher moisture retention. For example, at 20% of weight loss, sample prepared in Ti/P = 1/1 indicates 4.9 min; on the other hand, sample prepared in Ti/P = 3/2 indicates 7.7 min. Sample prepared in Ti/P = 3/2 has higher moisture retention than other samples. The moisture retention is caused from surface and pore of particles, particle size, surface condition of particles, and so on. From ICP results (Table 1), sample prepared in Ti/P = 3/2 indicates higher Ti/P ratio of precipitate than other samples. This ratio has influence on the surface of particles.

Table 2 Whiteness of samples prepared with titanium sulfate by color analyzer

Sample	Ti/P ratio under preparation condition	L^* without heating	L^* heated at 100 ℃
a	1/2	98.6	87.1
b	3/4	97.0	89.9
c	1/1	94.2	86.8
d	3/2	97.2	90.5
e	2/1	95.5	85.6
f	3/1	95.3	89.7

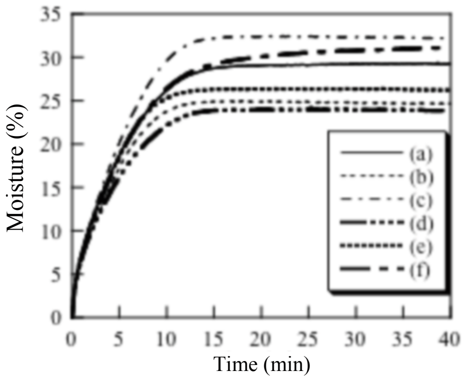

Fig. 6 Moisture retention of samples prepared in various Ti/P ratios: (a) 1/2, (b) 3/4, (c) 1/1, (d) 3/2, (e) 2/1, and (f) 3/1.

As described above, pigment with high smoothness spreads well on the skin. The powder smoothness is also important for cosmetics [12]. Table 3 shows the smoothness of samples prepared in various Ti/P ratios. Because sample prepared in Ti/P = 3/1 is obtained in small amount, the smoothness cannot be measured. Generally, for a cosmetic application, the suitable MIU and MMD values are smaller than 0.6 and smaller than 0.04, respectively. All samples indicate the suitable

Table 3 Smoothness of samples prepared with titanium sulfate

Sample	Ti/P ratio under preparation condition	Heating condition	MIU	MMD
a	1/2	Without heating	0.437	0.007
b	3/4	Without heating	0.550	0.009
c	1/1	Without heating	0.450	0.008
d	3/2	Without heating	0.500	0.010
e	2/1	Without heating	0.473	0.010
b	3/4	Heated at 100 ℃	0.507	0.006
c	1/1	Heated at 100 ℃	0.447	0.007

MIU and MMD values. The Ti/P ratio and heating condition have less influence on the smoothness in this work.

4 Conclusions

Titanium phosphates were synthesized from titanium sulfate and phosphoric acid. These titanium phosphates had less photocatalytic activity to protect the sebum on the skin. Samples without heating and those heated at 100 ℃ showed high reflectance in the range of visible light. Sample prepared in Ti/P = 3/2 had higher moisture retention than samples prepared in other Ti/P ratios. Titanium chloride used in previous works was difficult to treat because of the formation of smoke and undesirable precipitate. From the results obtained in this work, titanium sulfate was more suitable to obtain titanium phosphate as a white pigment for cosmetics.

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